Electronic Properties of Thin Film Organic Superconductors studied using Synchrotron Radiation-based Soft X-Ray Spectroscopies

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The goal of this program is to use synchrotron radiation-based soft x-ray spectroscopies to measure the electronic structure of organic superconductors. To accomplish this, we need to develop methods to synthesize thin films of organic superconductors using molecular beam deposition techniques. The primary spectroscopic probes used in this program are high resolution soft x-ray emission spectroscopy (SXE), resonant inelastic x-ray scattering, high resolution core and valence band photoemission spectroscopy, and soft x-ray absorption.

Figure 1 shows resonant SXE spectra from thin films of a simple organic semiconductor, copper phthalocyanine (CuPc). This experiment proves that our proposed method of minimizing beam damage in organic systems is feasible; see figure caption. We have measured states near the Fermi level in undamaged CuPc that, although predicted, have not been observed before. These results have recently been published: **J.E. Downes, C. McGuinness, P.A. Glans, T. Learmonth, D. Fu, P. Sheridan, and K.E. Smith, Chem Phys. Lett. 390, 203 (2004)**

We have also made preliminary progress in the *in-situ* synthesis of thin film organic superconductor-type materials based on ET, where ET stands for the organic donor molecule of bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF). Figure 2 shows Scanning Electron Microscope (SEM) pictures from thin films of pure ET and of nominal $(ET)_2SF_5CH_2CF_2SO_3$. Such films have never been synthesized before, and will allow us to apply our synchrotron-based probes without concern for beam damage.

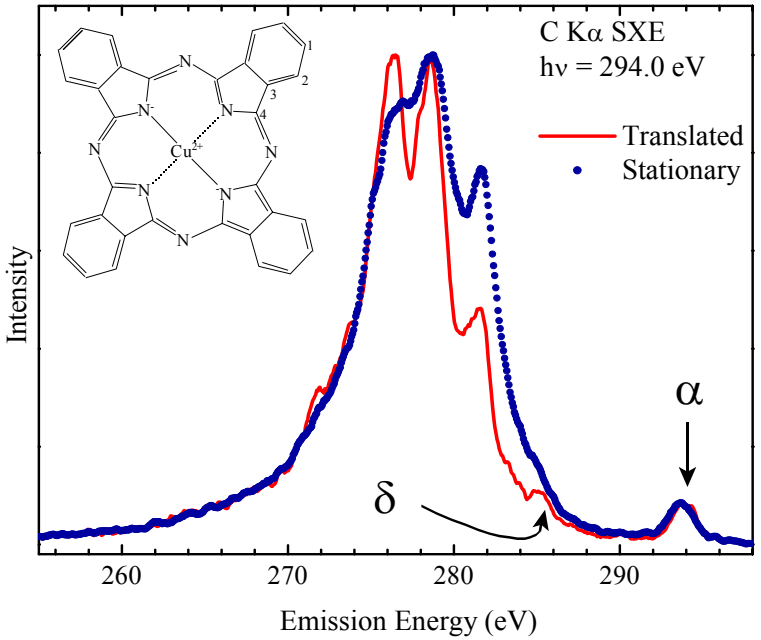

Figure 1: Resonant SXE spectra reflecting the C *2p* PDOS in CuPc for both translated and stationary films. High resolution SXE measurements require a small photon spot (circa 40 μm) with a high photon flux (10^{13} ph/s) on the sample, and long collection times (30 - 60 min). This combination can lead to significant beam induced damage in organic systems. We have solved this problem by continuously translating the films in front of the beam (at 40 μm/s) as the spectra are being recorded. Significant differences in the measured electronic structure of identical films when stationary or translated are visible in the figure.

Organic superconductors have been the subject of intense study for many years due both to the challenge they pose to our understanding of the physical properties of complex solids and due to technological interest in developing advanced carbon-based electronic devices. There is a serious lack of detailed spectroscopic measurements of the electronic structure, primarily due to severe radiation damage problems, and difficulties in preparing ordered and clean surfaces. This program uses a powerful combination of high resolution synchrotron radiation-based soft x-ray spectroscopies to measure the electronic structure of organic superconductors. We intend to solve the beam damage and surface problems associated with earlier studies of single crystals by growing thin films of these materials *in-situ*, and continuously translating the films in front of the synchrotron radiation beam as spectra are recorded. Program goals are to develop organic molecular beam deposition methods for the *in-situ* synthesis of ordered thin films of these superconductors and to make definitive measurements of the electronic properties of the films. This project will have a significant impact on the education of students and postdoctoral research associates by exposing them to a highly collaborative research environment at national user facilities. They will be educated in the physics of novel organic materials, and in the application of synchrotron radiation spectroscopies in their study.

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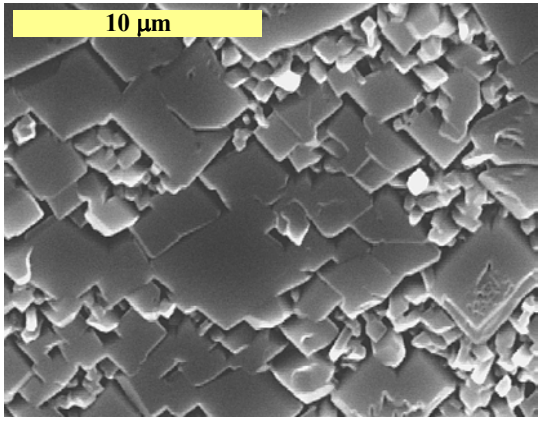
Educational Activities:
This research program involves one undergraduate student (Cian O'Donnell), one graduate student (Yufeng Zhang) and one postdoctoral research associate (Dr. Shancai Wang). Note also that the PI has finished a two year appointment as the first Academic Director of the Center for Excellence in Teaching at Boston University. Furthermore, the PI was named the 2001 Massachusetts Professor of the Year by the Carnegie Foundation.

Infrastructure Impact:
This program uses a custom designed ultra high vacuum organic molecular beam deposition chamber, attached to our multi-technique spectrometer system based at the National Synchrotron Light Source (NSLS). The spectrometer system features both a high resolution angle resolved photoemission spectrometer (100 mm Scienta), and a high resolution soft x-ray emission spectrometer. This is a unique combination of growth and characterization capabilities, and is available to other scientists through the General User Program at the NSLS.



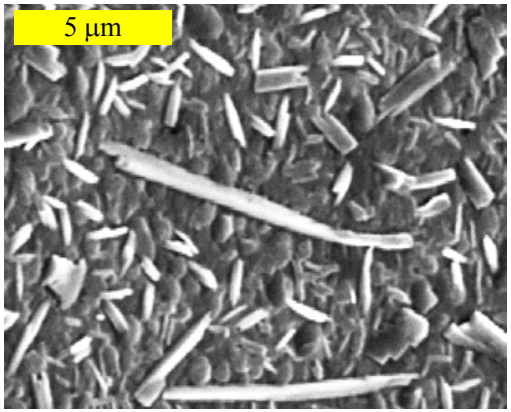


Figure 2: The left panel shows an SEM picture of pure ET grown on an NaCl substrate, displaying clear two dimensional platelets. The right panel shows the SEM scan of a film (grown on a KBr substrate) resulting from the co-evaporation of ET and pentafluorothioethylsulfonic acid ($SF_5CH_2CF_2SO_3H.H_2O$). The basic reaction we seek to initiate is $4(ET) + 2(SF_5CH_2CF_2SO_3H) \rightarrow 2((ET)_2SF_5CH_2CF_2SO_3) + H_2$. Quasi-one dimensional crystallites are visible in the SEM image on the right, indicating that material similar to bulk $(ET)_2SF_5CH_2CF_2SO_3$ is being obtained. The room temperature resistance of these films is essentially the same as that measured for equivalent single crystals. Spectroscopic studies of these types of films are underway.